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Ab initio calculations have been performed on adsorption of H_2O molecules on Ti-doped silicon clusters $TiSi_n$ using the ultrasoft pseudopotential method within the generalized gradient approximation. Our results show that for $n=13$ and larger clusters adsorption of H_2O on $TiSi_n$ could be difficult due to low binding energies. All these clusters have cage structures with the metal atom surrounded by the silicon atoms. On the other hand, smaller clusters with $n<13$ have the metal atom partially covered by Si atoms in a basket structure so that it is available for reaction with a water molecule. This leads to significantly higher binding energies of a water molecule on such clusters. These results are in excellent agreement with the available experimental data, which show significant decrease of H_2O adsorption on clusters with $n>12$.

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Currently, metal (M) encapsulated silicon clusters are attracting much attention[1–14] because of their interesting properties and structures. These could serve as building blocks for nanomaterials and miniature devices. Cage structures, especially fullerene, cubic, and Frank-Kasper type have been predicted for MSi_n ($n=14-16$) by Kumar and Kawazoe[1] with their unique characteristics. Subsequently, many theoretical studies have been made to determine the properties of clusters with $M=$Cr,[2–4] Fe,[1,5,6] and other M atoms.[7–10] In addition, large abundances have been obtained for 15 and 16 Si atom clusters with one M atom[11,14] and low reactivity of MSi_{12}, $M=$Cr, Mo, W has been obtained with hydrogen.[3,12] Recently, adsorption behavior and electron affinities of Ti-doped clusters have been studied which are important for the understanding of their stability as well as for their usage. Kumar *et al.*[13] have studied the ionization potentials and electron affinities of $M@Si_{16}$, $M=$Ti and Zr clusters. Ohara *et al.*[14] have reported the experimental results of not only the mass spectra but also the adsorption of H_2O molecules on Si_nTi clusters. These studies could also serve as important benchmarks to understand the structures of MSi_n clusters.

The results of these experiments show that adsorption of H_2O on $Ti@Si_n$ clusters could be found only up to $n=12$. For larger clusters, the reaction ratio decreases significantly and from $n=15$ onwards it becomes almost zero. Considering the well known high reactivity of H_2O with Ti, the vanishingly small adsorption of H_2O molecules on $TiSi_n$ clusters with $n>12$ is thought to be due to the encapsulation of Ti by Si atoms so that Ti atom is not accessible to H_2O molecules for reaction. However, this idea could not explain all the experimental results *a priori*. For example, a hexagonal prism structure can exist for $n=12$ similar to the one[3,12] for WSi_{12}. As the hexagonal faces are not capped, it is possible that H_2O could interact with Ti by intruding into the relatively open hexagonal rings. If it can, the experiments are not the proof for the formation of cage structures. Moreover, at the outset it is not clear if the Si atoms should be weakly interacting with H_2O if a cage is formed. The atomic structures of smaller clusters with $M=$Ti have not yet been understood. In order to understand the interaction of H_2O with $TiSi_n$ clusters, the determination of the structures of $TiSi_n$ clusters in the wide range of sizes under the same calculation conditions is indispensable. So far theoretical studies are mostly on a few selected sizes. Therefore, we have first performed calculations for determining the lowest energy structures of $Ti@Si_n$ clusters with $n=8-16$. Based on these results, further calculations have been done on adsorption of a H_2O molecule on $TiSi_n$ clusters.

The calculations are performed using the *ab initio* ultrasoft pseudopotential method,[15,16] within the spin-polarized generalized gradient approximation of Perdew and Wang[17] for the exchange-correlation energy. A simple cubic supercell with size 15 Å for $n=8-14$ and 18 Å for other larger clusters is used with periodic boundary conditions. The Brillouin zone is represented by the Γ point. For Si and O we consider only the outer valence electrons, but for Ti we also included $3p$ atomic core states as valence states. The structural optimizations have been performed using the conjugate gradient method such that the residual force on each ion was less than 0.001 eV/Å. The total energy has been calculated up to an accuracy of 0.0001 eV. In order to determine the lowest energy structures we used several candidates as initial guesses. Although one cannot still be completely sure of the minimum energy structures, we believe that our results should represent lowest energy structures. This belief is further supported by the good agreement with experiments of the adsorption behavior of a water molecule. Here we report the structures of $TiSi_n$ briefly from the point of view of the adsorption of H_2O. A detailed discussion of the low lying structures and the growth behavior has been given in Ref. 18. While under the experimental conditions of finite temperatures, there could be more than one isomer present for some clusters if the energy difference is small and vibrational contribution to entropy as well as zero point energy may affect the ordering of free energies, we have considered primarily the lowest energy structures. We believe that our studies demonstrate sufficiently clearly the main findings of the experiments.

Figure 1 shows the lowest energy structures of $TiSi_n$ [(a)–(i)] and two interesting isomers [(j) and (k)] for $TiSi_{12}$ and $TiSi_{13}$, respectively. These can be classified into basket and

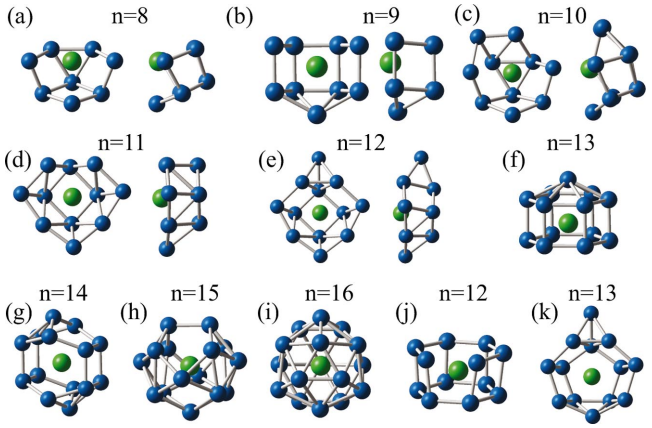

FIG. 1. (Color) (a)–(i) The lowest energy structures of $TiSi_n$ ($n=8-16$) with (j) and (k) as the local minimum structures for $TiSi_{12}$ and $TiSi_{13}$, respectively. Ti atom is shown by a bigger ball (green).

cage structures. As seen in Fig. 1, the most favorable structures for $n=8-12$ are basket type. In these clusters the Ti atom is partially covered with Si and therefore it could interact with H_2O. Furthermore, we find that a hexagonal prism structure is not the lowest energy structure for $TiSi_{12}$. It prefers a basket-type structure and it is the largest cluster for $Ti@Si_n$ with the basket structure. Figure 1(j) shows a hexagonal prism-like cage structure for $n=12$, but one Si-Si bond is quite elongated (not bonded in Fig. 1), with the bond length of 3.00 Å. This can exist as a local minimum with 0.273 eV higher energy as compared to the basket isomer. The larger atomic radius of Ti as compared to Cr or W could be a reason for the opening of this hexagonal prism structure besides the fact that the number of electrons in the case of Ti is different, and this could also lead to a different structure to be of the lowest energy. We also calculated a hexagonal antiprism structure and it lies 0.680 eV higher in energy. Therefore, it is also a local minimum isomer. From these results we conclude that cage structures are not suitable for $n=12$. Cage structures are, however, formed for $n>12$ (Fig. 1). We calculated a basket isomer for $n=13$ [Fig. 1(k)] and it lies 0.878 eV higher in energy than the cage isomer. An interesting point is that $n=13$ and 14 have open (not capped) hexagonal rings so that H_2O molecule might intrude into the clusters to interact with Ti. Thus, the possibility of adsorption of H_2O molecules could not be determined only by these structures.

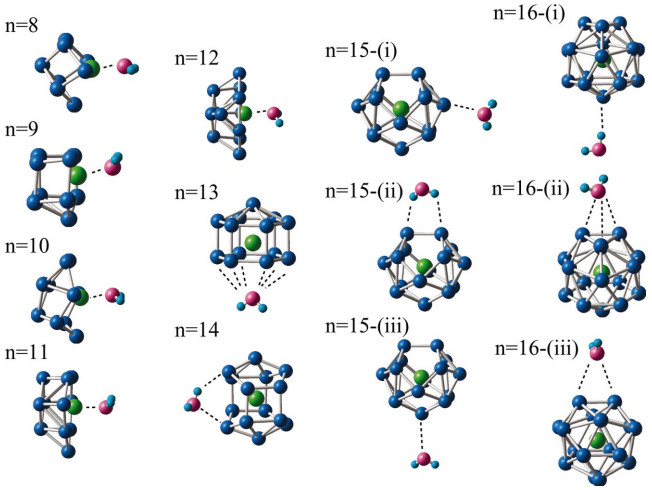

FIG. 2. (Color) Optimized arrangements of H_2O interacting with $TiSi_n$ clusters. For $n=15$ and 16, three different approaches of water molecule to the cluster are shown. The nearest bonds between the H_2O and the cluster are shown by dashed lines. The small (big) balls represent H (O) atoms in the H_2O molecule.

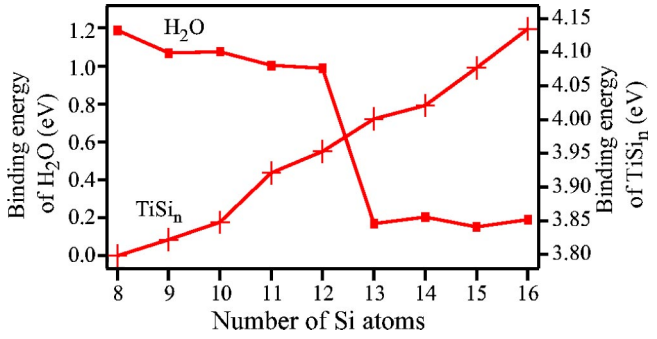

FIG. 3. Interaction energies (left scale) between $TiSi_n$ and H_2O ($n=8-16$). The atomic arrangements for $n=15$ and 16 are shown, respectively, as 15-(i) and 16-(i) in Fig. 2 which have the largest interaction energy in each size. The right scale shows the binding energy per atom of $TiSi_n$ clusters.

As in experiments of H_2O adsorption all clusters are positively charged, we also determined[18] the structures of cation clusters following the results of the neutral clusters. It is found that the structural differences between the neutral and cation clusters are not significant. For $n=12$ the energy difference[18] between the cage and the basket isomers is not large (0.273 eV) and we also studied cations of both these isomers. Our calculated energy difference between the cations is 0.387 eV and the basket isomer remains more stable than the cage isomer. More details of these studies will be published separately.[18] The calculations of adsorption of H_2O on $TiSi_n$ have been performed by initially putting an H_2O molecule with O facing the Ti atom of the lowest energy isomer of $TiSi_n$ for $n=8-12$ (basket structures) and in front of the center of the open hexagonal ring for $n=13$ and 14 cage isomers. For $n=15$ and 16 cage isomers there are no such open sites for the H_2O molecule to adsorb. Therefore,

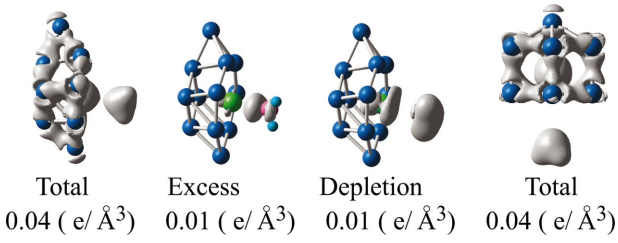

FIG. 4. (Color) Electronic-charge density isosurfaces for $TiSi_n$ ($n=12$ and 13) interacting with H_2O. Excess and depletion charges for $TiSi_{12}$ are calculated from the difference between the charge of $TiSi_n$ interacting with H_2O and the sum of the charges of the isolated $TiSi_n$ and H_2O.

TABLE I. Binding energy (BE) per atom for $TiSi_n$ clusters, optimized distances between Ti and O ($d_{Ti\text{-}O}$), and interaction energies (E) between $TiSi_n$ and H_2O. The three values for $n=15$ and 16 correspond to three configurations of H_2O. In the case of $n=13$, oxygen is nearly equidistant from Si and Ti atoms, but for $n=14-16$, the Ti-O bond is quite long and the interaction is actually with silicon atoms.

n	BE/atom (eV)	Optimized $d_{Ti\text{-}O}$ (Å)	E (eV)
8	3.798	2.14	1.188
9	3.822	2.16	1.069
10	3.848	2.16	1.076
11	3.921	2.20	1.004
12	3.953	2.19	0.989
13	4.001	3.78	0.169
14	4.021	4.52	0.204
15-(i)	4.077	5.64	0.152
15-(ii)	4.077	5.80	0.137
15-(iii)	4.077	6.03	0.078
16-(i)	4.135	6.26	0.189
16-(ii)	4.135	5.71	0.156
16-(iii)	4.135	5.87	0.156

three directions of approach have been selected for the H_2O molecule. The optimized arrangements and the distances between Ti and O are shown in Fig. 2 and in Table I, respectively.

In the basket isomers an H_2O molecule stays near the cluster and the distance between Ti and O after the optimization lies in the range of 2.14 to 2.20 Å. In the most important sizes of $n=13$ and 14, very weak or no adsorption could be found in experiments. It is found that in these cases the H_2O molecule moves away from the cluster and the final converged Ti-O bond lengths in $n=13$ and 14 are large (3.78 and 4.52 Å, respectively) and the interaction is more with the Si atoms. For $n=13$, the Si-O bond lengths are in the range of 3.65–3.71 Å, which are nearly equal to the Ti-O bond. However, the change in the position of Ti atom after adsorption of H_2O is quite small. Therefore, we conclude that interaction of H_2O is predominantly with Si atoms. In the case of $n=14$, the bare $Ti@Si_{14}$ cage structure is quite distorted and O interacts with one Si atom such that the Si-O bond length is shorter (2.93 Å). In addition, one H interacts with a Si atom and the Si-H bond length is 2.61 Å. Accordingly in this case the interaction of H_2O is slightly stronger. This leads to a slight enhancement in the interaction energy. For $Ti@Si_{15}$ and $Ti@Si_{16}$ only weak interaction with Si atoms has been found for all three approaching directions, as expected. However, after optimization the directions of H_2O to the clusters are not the same. As seen in Fig. 2, for $Ti@Si_{15}$ we considered two top sites and one bridge site as initial configurations with, O facing the cluster. In the two cases of top sites O interacts with the cage atoms [15-(i) and 15-(iii)], while in the case of the bridge site [15-(ii)], the two H atoms interact with the Si bridge atoms. The Si-H bond lengths are 2.92 and 3.15 Å. The O-Si bond lengths are 2.83 and 3.35 Å for isomers 15-(i) and 15-(iii), respectively. For $Ti@Si_{16}$, O points to the cluster side when it is on a bridge site (Si-O bond lengths 3.50 Å) joining two Si hexagons [Fig. 2 (16-iii)] or on a triangle (Si-O bond lengths 3.48–3.58 Å) joining three Si hexagons [Fig. 2 (16-ii)]. However, when H_2O is placed on top of a capping atom (of Si hexagons), then H points towards the cluster, as shown in Fig. 2 (16-i) with Si-H bond length of 2.70 Å. The Si-H as well as Si-O bond lengths in these clusters are much longer as compared to the covalent bond length of about 1.5 Å for Si-H and 1.65 Å for Si-O. This different result indicates weak interaction between H_2O and the clusters.

In order to further quantify the interaction, we estimate the interaction energy from $E(TiSi_n)+E(H_2O)-E(TiSi_n+H_2O)$. It is given in Table I and Fig. 3. The interaction energy in the basket isomers ($n=8-12$) is about 1 eV and except for $n=8$, it lies in a quite small range, the decrease being only 0.080 eV in going from $n=9$ to $n=12$. Therefore, adsorption of H_2O is energetically favorable for $n=8-12$, with a small decrease in the interaction energy as the size increases. On the other hand, the stability of clusters becomes better with an increase in size, as can be seen in Fig. 3. After $n=16$, there is a decrease in the binding energy.[18] For $n=13-16$ the interaction energies of H_2O are less than about 0.20 eV and there is no significant difference with a change in n. It increases a little from $n=13$ to $n=14$, as also discussed above, and then decreases again. In experiments, a little adsorption has been found only in $n=13$ and 14 and there is also a little increase in going from 13 to 14.

From the above, it is therefore clear that our results are in excellent agreement with reported experiments and show that H_2O adsorption could occur up to $n=12$. The experimental results also show some interesting behavior of the reaction ratio, which agrees completely with our calculations. First, the experimental ratio decreases in going from $n=7$ to $n=12$, with the value changing from 0.8 to 0.4. Besides the small decrease in the interaction energy that we obtained in our calculations (Fig. 3), the structure is also likely to play an important role in adsorption. The most favorable structures of $TiSi_n$ ($n=8-12$) are basket structures and with the increase in size, Ti atom loses its exposed part more and more, and finally at $n=12$, half of Ti is completely surrounded by Si atoms. Therefore, in such a structure, adsorption sites for H_2O become more limited so that the reaction ratio could decrease more significantly. The second interesting point is that in the experiment $n=13$ and 14 have still some reaction, while from $n=15$ the adsorption ratio is almost zero. As seen in Fig. 3, the inertness for adsorption is the same in $n=13-16$. However, considering the large structural change between $n=12$ and 13, the basket isomer for $n=13$ and 14 could exist even though cage isomer has an energetic advantage. The third interesting aspect is seen in $n=14$, which has larger adsorption ratio as compared to $n=13$. Our calculated results also show a slight increase in the interaction energy and this is likely to be responsible for an increase in the reaction ratio. In addition, $n=14$ cage isomer has two open hexagonal rings, while $n=13$ has one. A similar slight increase of the interaction ratio is seen for $n=10$ and there is a corresponding increase in the interaction energy as well.

$n=13-16$ clusters also have large highest occupied-lowest unoccupied molecular orbital gaps (more than 1.4 eV) and for $n=15$ and 16, it has values of 1.58 and 2.36 eV, respectively. This is also likely to be the reason for their inertness.

The bonding nature between $TiSi_n$ and H_2O is important to understand adsorption behavior of H_2O molecules. To analyze the interaction we have plotted the electronic-charge density distributions in Fig. 4 for $n=12$ and 13 as representative examples of the adsorbing and not-adsorbing clusters, respectively. For $n=12$ we have shown the total, excess, and depletion of charge with the excess and depletion charges defined as the differences between the interacting system $TiSi_n+H_2O$ and the sum of charges of the isolated $TiSi_n$ cluster and the H_2O molecule. From the total charge density distribution one finds strong covalent-like Si-Si bonds and some charge accumulation between Ti and H_2O. There is a small charge transfer from the vicinity of Ti and H ions to the region between the Ti and O ions. This charge transfer occurs in quite limited space so that the stability and the atomic structure of $TiSi_n$ cluster is not affected significantly. For $n=13$ we have shown only the total charge density distribution as the excess and depletion charge distributions are too small (less than 0.01 $e/Å^3$). Therefore, the charge transfer as well as the interaction between $TiSi_n$ cluster and H_2O molecule is rather weak, as expected.

The above description of interaction of water is corroborated by the orbital energies shown in Fig. 5. As one can see, the orbital energies of the $TiSi_{12}$ cluster get shifted upwards, while those of H_2O molecule shift significantly to higher binding energies indicating significant covalent bonding between water and the silicon cluster. On the other hand for $TiSi_{13}$, this shift is quite small, supporting the weak interaction.

In summary, we have reported *ab initio* calculations of the adsorption of a H_2O molecule on titanium-doped silicon clusters of different sizes. The equilibrium structures and interaction energies have been obtained. It is found that $TiSi_n$ clusters form a cage structure from $n=13$ onwards so that H_2O adsorption could occur only up to $n=12$, for which basket structures are preferred with Ti partially exposed and being available for interaction. These results are in excellent agreement with reported experimental results in which a little adsorption can be found beyond $n=12$. The interaction between $TiSi_n$ and H_2O is evaluated by the calculation of the interaction energy. It clearly shows a decrease from $n=12$ to

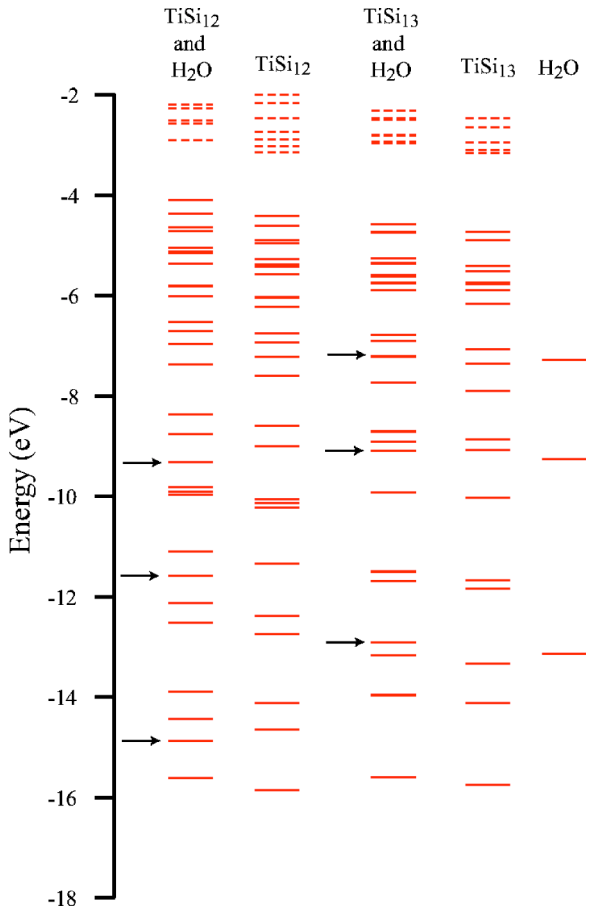

FIG. 5. Electronic levels for $TiSi_n$ ($n=12$ and 13) before and after interaction with H_2O and the H_2O molecule. Broken lines show the unoccupied levels. The arrows show the position of the H_2O levels after adsorption.

$n=13$ and very small interaction energies for $n=14-16$, supporting their inertness and cage structures, in complete agreement with experiments.

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[1] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **87**, 045503 (2001); **91**, 199901 (2003); V. Kumar, Eur. Phys. J. D **24**, 227 (2003); V. Kumar, Comput. Mater. Sci. **30**, 260 (2004).
[2] V. Kumar and Y. Kawazoe, Phys. Rev. B **65**, 073404 (2002); V. Kumar and Y. Kawazoe, Appl. Phys. Lett. **83**, 2677 (2003); V. Kumar *et al.*, Nano Lett. **4**, 677 (2004).
[3] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. **90**, 055502 (2003).
[4] S. N. Khanna *et al.*, Phys. Rev. Lett. **89**, 016803 (2002).
[5] S. N. Khanna *et al.*, Chem. Phys. Lett. **373**, 433 (2003).
[6] G. Mpourmpakis *et al.*, Phys. Rev. B **68**, 125407 (2003).
[7] J. Lu and S. Nagase, Phys. Rev. Lett. **90**, 115506 (2003).
[8] F. Hagelberg *et al.*, Phys. Rev. B **67**, 035426 (2003).
[9] P. Sen and L. Mitas, Phys. Rev. B **68**, 155404 (2003).
[10] G. Mpourmpakis *et al.*, J. Chem. Phys. **119**, 7498 (2003).
[11] S. M. Beck, J. Chem. Phys. **90**, 6306 (1989).
[12] H. Hiura *et al.*, Phys. Rev. Lett. **86**, 1733 (2001).
[13] V. Kumar *et al.*, Phys. Rev. B **68**, 155412 (2003).
[14] M. Ohara *et al.*, Chem. Phys. Lett. **371**, 490 (2003).
[15] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996); G. Kresse and J. Hafner, J. Phys.: Condens. Matter **6**, 8245 (1994).
[16] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[17] J. P. Perdew and Y. Wang, Phys. Rev. B **45**, 13244 (1992).
[18] H. Kawamura, V. Kumar, and Y. Kawazoe, Phys. Rev. B (to be published).